PATENT SPECIFICATION

NO DRAWINGS

Inventor: THOMAS HUNT

1,026,878

1,026,878

Date of filing Complete Specification Jan. 18, 1963.

Application Date Jan. 18, 1962. No. 1809/62.

Complete Specification Published April 20, 1966.

Index at acceptance.—C2 C(2B46A2, 2B46A3, 2B46G1, 2B46G5, 3A10E4B2, 3A10E4B3, 3A10E4B4, 3A10E4C, 3A10E5F1C, 3A10E5F1D, 3A10E5F2A); C4 A(2, 9A, 9B, 9C)

Int. Cl.:—C 07 c//C 09 d

COMPLETE SPECIFICATION

Aqueous Surface Coating Compositions

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to resins, hereinafter referred to as surface coating resins, from which improved aqueous surface coating compositions can be obtained. In particular it relates to a process for the production of aqueous surface coating compositions that give rise to films having improved water resistance after air drying.

It is known that surface coating resins can be prepared by reacting drying oils with unsaturated acids such as maleic acid to produce a product which can be dissolved or dispersed in an aqueous alkali solution to give a surface coating composition. Such compositions have many useful properties but the films formed by applying them to suitable surfaces have very poor water resistance after air drying.

An object of the present invention is to provide surface coating resins based on reaction products of the type described above which give rise to surface coating compositions having improved drying characteristics and capable of forming films having improved water resistance.

According to the present invention the process for the production of an aqueous surface coating composition comprises partially esterifying the reaction product of a compound functioning as an unsaturated oil and a compound having an available residue of an acyclic, olefinic carboxylic acid, both compounds as herein defined, with a monohydric alcohol, the esterified product containing sufficient carboxyl groups to ensure subsequent solution, and dissolving said esterified product in an aqueous solution of a base.

By a compound functioning as an unsaturated oil is meant throughout this specification the oil itself which consists of or comprises a triglyceride ester of an unsaturated fatty acid having at least 12 carbon atoms in the carbon chain containing the unsaturation, or said unsaturated fatty acid, or an ester thereof with a mono- or polyhydric alcohol other than glycerol.

Examples of unsaturated oils are tung, oiticicia, linseed, soya, cotton seed, dehydrated castor, perilla, and unsaturated fish oils. Tall oil fatty acids and acids obtained by hydrolysis from these unsaturated oils are suitable unsaturated fatty acids for use in the process of the present invention. Examples of mono or polyhydric alcohols from which suitable esters can be obtained are methyl alcohol and the polyglycols.

Minor amounts of synthetic and naturally occurring dienes, e.g. cyclopentadiene, butadiene, gum rosin, and myrcene, may be introduced to modify the reaction product of the oil and the carboxylic acid.

By a compound having an available residue of an acyclic olefinic carboxylic acid is meant throughout this specification a mono- or poly- as carboxylic acid having less than 10 carbon atoms in any carbon chain, no cyclic groups and olefinic unsaturation, and in the case of polycarboxylic acids, their anhydrides. The preferred acids are dicarboxylic acids. Suitable acyclic, olefinic polycarboxylic acids are maleic acid, fumaric acid, aconitic acid, itaconic acid and alkyl-substituted maleic acids having less than ten carbon atoms in any carbon chain. Suitable acyclic, olefinic monocarboxylic acids are acrylic or methacrylic acid. Citric acid

[*Price* 4*s.* 6*d.*]

when subjected to the conditions under which citraconic anhydride or itaconic acid is produced (Bernthsen, Textbook of Organic Chemistry (1923) pages 250 to 256) can also be employed.

Maleic acid is the preferred acyclic, olefinic carboxylic acid and it is preferred to employ it in the form of maleic anhydride.

The conditions for the reaction of the compound functioning as the unsaturated oil and the compound having an available residue of an acyclic olefinic carboxylic acid are known and the reaction products for use in the process of the present invention may be prepared by these known procedures. A sufficient quantity of the compound having an available residue of an acyclic olefinic carboxylic acid is employed to ensure that the final product according to the present invention is water soluble. By water soluble is meant throughout this specification that the product dissolves in water containing a base, for example a soluble alkali metal hydroxide or an ammonia base of the class which consists of ammonia and primary, secondary and tertiary aliphatic amines. When the compound having the available residue of an acyclic olefinic carboxylic acid is maleic acid or maleic anhydride the proportion by weight of the maleic acid compound to the compound functioning as an unsaturated oil can be in the range 5 to 50 parts of maleic acid compound to 100 parts of compound functioning as an unsaturated oil.

Preferably the reaction between the compound functioning as the unsaturated oil and the compound having an available olefinic carboxylic acid residue is effected by heating the reactants together for an extended period of time at a temperature of at least 110°C and commonly below 300°C. until substantially all of the compound having the available olefinic carboxylic acid residue is chemically combined with the compound functoning as the unsaturated oil. When maleic anhydride is employed to react with linseed oil, the preferred reaction temperature is between 200 and 240°C. and the reaction is carried out under reflux conditions in order to return to the mixture any maleic anhydride which boils or sublimes off. Such reactions suitably employ from 10 to 45% maleic anhydride on the total weight of linseed oil and maleic anhydride.

The preferred monohydric alcohols are the aliphatic and cyclo-aliphatic alcohols containing from 1 to 18 carbon atoms per molecule. The alcohols may be saturated or unsaturated.

The quantity of the monohydric alcohol used to esterify the reaction product is arranged so that only partial esterification of the carboxylic groups in the reaction product takes place and so that the resultant esterified product is soluble in an aqueous solution of a base. Minor proportions of polyhydric alcohols can be present in the reaction mixture.

This is effected by arranging that the number of hydroxyl groups added is less than the number of carboxyl or potential carboxyl groups in the reaction product of the compound functioning as an unsaturated oil and the compound having an available olefinic carboxylic acid residue.

The esterification of the reaction product of the compound functioning as an unsaturated oil and the compound having an available residue of an acyclic olefinic carboxylic acid with the monohydric alcohol can be carried out under normal esterification reaction conditions. Most suitably these involve heating the reaction product and the alcohol to temperatures in the range 100—250°C. under nitrogen to the desired acid value. Entrainment with an organic solvent such as xylol can be employed, to remove the water of reaction.

The surface coating resins produced according to the process of the present invention are water soluble if a sufficient number of free or potentially free carboxylic groups are present. As stated above by "water soluble" is meant that the surface coating resin dissolves in water containing a base. It is preferred to use a volatile base such as ammonium hydroxide or a volatile organic amine such as triethylamine to bring about or increase the water solubility of the products of the present invention, because it is to a large extent driven off as free base with the evaporation of water during the formation of the surface coating film from compositions containing surface coating resins according to the present invention.

Aqueous surface coating compositions prepared according to the present invention can be used as the bases for valuable paints and the like. The usual metallic driers, fillers, pigments, etc. are generally added.

The following example illustrates the preparation of a surface coating composition according to the present invention.

Example

Preparation of Maleinised Linseed Oil

Varnish linseed oil (1064 grams) and maleic anhydride (336 grams) were heated and stirred at 220°C. for 7 hours under nitrogen. The maleinised oil was then cooled to room temperature.

Partial Esterification of the Maleinised Oil

1800 grams of the maleinised oil described above and 675 grams of cyclohexanol were heated and stirred at 150°C. under nitrogen for one hour. The temperature was raised to the reflux and water of reaction removed by entrainment, the excess cyclohexanol serving as an entraining solvent. When the acid value had fallen to 60—65, excess cyclohexa-

nol was distilled. The resin was finally cooled to room temperature.

An aqueous solution of the ester triethylamine salt was prepared by stirring the ester (1730 parts by weight) with water (1518 parts by weight) and triethylamine (212 parts by weight).

Films of this solution containing cobalt naphthenate (0.12% cobalt on the weight of the ester) air dried to give water resistant tough glossy films.

WHAT WE CLAIM IS:—

1. A process for the production of an aqueous surface coating composition which comprises partially esterifying the reaction product of a compound functioning as an unsaturated oil and a compound having an available residue of an acyclic, olefinic carboxylic acid, both compounds as herein defined, with a monohydric alcohol, the esterified product containing sufficient carboxyl groups to ensure subsequent solution, and dissolving the esterified product in an aqueous solution of a base.

2. A process as claimed in claim 1, wherein the compound functioning as an unsaturated oil is linseed oil or linseed oil fatty acids.

3. A process as claimed in claim 1 or 2 wherein the compound having an available acyclic, olefinic carboxylic acid residue is a dibasic acid or the anhydride thereof.

4. A process as claimed in claim 3, wherein the compound is maleic anhydride.

5. A process as claimed in any of the preceding claims wherein the monohydric alcohol is an aliphatic or cyclo-aliphatic alcohol containing from 1 to 18 carbon atoms per molecule.

6. A process for the production of an aqueous surface coating composition substantially as described in the example.

7. Aqueous surface coating compositions when prepared by a process as set forth in any of the preceding claims.

J. N. GAMMON,
(Agent for the Applicants),
Great Burgh, Epsom, Surrey.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1966.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.